

Appl. No. 10/535,050
Amdt. Dated July 27, 2009
Amdt. following telephone interview of July 23, 2009

Amendments to the Specification:

Reference here is to the paragraph numbering used in the published Patent Application US 2006/0127299 A1.

Please replace paragraph [0005] with the following amended paragraph:

[0005] The present invention provides a process for the manufacture of carbon nanostructures, the carbon nanostructures being selected from carbon nanotubes and carbon nano-onions, the method comprising the steps of injecting a carbon-containing gas substance via a fast quenching nozzle attached to a high enthalpy electrode-generated direct current thermal plasma torch into a plasma flame generated from a plasma forming gas to provide atomic carbon, which in the presence of in-situ *in situ* generated nanometer sized metal catalyst particles that act as nucleation points for the growth of carbon nanostructures, produce the carbon nanostructures, and collecting the carbon nanostructures.

Please replace paragraph [0026] with the following amended paragraph:

[0026] A high enthalpy plasma torch an example of which is found in U.S. Pat. No. 5,147,998 can be used to generate the plasma. At the torch_1 outlet is attached a water-cooled nozzle_2 (see FIG. 1) for the injection of the carbon-containing gas feed_4. Experiments were carried out using tetrachloroethylene (TCE, C₂Cl₄) as the carbon source. The invention however is not limited to this gas as other mixtures of hydrocarbon have been shown to yield the fullerene precursor molecules. For example, see U.S. Pat. Nos. 5,395,496; 5,985,232; 6,162,411; 6,083,469; 6,099,696; 6,350,488 B1; 6,261,532 B1; 6,303,094 B1; 6,221,330 B1; 6,331,209 B1; and 6,333,016 B1 for examples of other gases and mixtures thereof. Thus various carbon halides can be used, as can various

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hydrocarbons. Typically, the carbon-containing gas may be characterized generally as a C₁-C₆ compound having as hetero atoms H, O, N, S or Cl, optionally mixed with hydrogen and mixtures thereof. The carbon-containing gas was carried to the nozzle and injected using a transporting gas such as helium or argon. The transporting gas is typically referred to as the carrier gas. Experiments described herein for CNT growth were made both with helium and argon gas. CNT production with argon (see FIG. 17) has an important advantage of lower cost of operation. Typically, but not necessarily, the transporting gas is the same type as that used as the main plasma forming gas 5 inside the plasma torch. The method described above and illustrated schematically in FIG. 1 is based on the method described in U.S. Pat. No. 5,395,496 for fullerene production. The electrode material in contact with the electric arc inside the plasma torch constitutes, through the arc erosion process, the source of material for the production of nano-particles of catalyst. The torch design used in the tests is based on U.S. Pat. No. 5,147,998 with tungsten as the electrode surface material. Alternatively, fine metal particles can be injected along with the carbon in the carrier gas or by using a separate injection line 11 in the nozzle as shown in FIG. 2. Alternatively, metal catalyst injection 12 can also be made downstream of the plasma torch-nozzle assembly using powders or metal samples melted and vaporized by the strong heat flux of the plasma flame as shown in FIG. 3A. Alternatively, metal catalyst nanoparticles can be added in the liquid carbon precursor and injected either downstream of the plasma torch. Alternatively, metal catalyst nanoparticles added in the liquid carbon precursor can be injected directly in the plasma when using an injection probe inserted in an inductively coupled thermal plasma torch (TP-ICP) instead of a DC plasma torch. The plasma torch may be attached to a synthesis reactor 17 with water-cooled walls 7 and an off gas cooling system 8 as illustrated in FIGS. 1 and 4. The pressure in the reactor can be controlled between 200 Torr and 800 Torr. Peripherals may be attached to the reactor and may be selected from units for off gas cleaning,

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pumping, cooling, control and electrical power supply for the plasma torch. Inside the reactor is a provision for product recovery on a water-cooled plate 10 facing the plasma torch at some adjustable position. Provisions to control the temperature profile and residence time in some given temperature zone can be added in the main chamber through the use of an inner enclosure surrounding the plasma jet. A hollow graphite cylinder 30 cm long is used as the inner enclosure in the present embodiment of the invention (see FIG. 3B).

Please replace paragraph [0027] with the following amended paragraph:

[0027] In the experiments described herein, tungsten electrodes were used to generate the nano-particles of catalyst. The very high boiling point of tungsten (5660°C.) results in the metal particles being generated directly within the nozzle, and as the nearby area of the nozzle wall has a temperature typically in the range of 1000-1500°C., the resulting fast quench of the metal vapor induces nanometer size particle nucleation. In such a scenario, an significant amount of long CNT structures 35 are produced directly on the nozzle walls as seen in FIG. 5, as this region corresponds to a good catalyst particle nucleation zone from the strong thermal gradients occurring close to the nozzle 34 wall. Also, the nucleation of catalyst particles from the thermal gradients generated by the cold TCE injection (compared to the hot plasma) also occurs in the main stream. These particles exit the plasma torch 36 and enter the main reactor chamber for CNT growth in the gas phase. A change in electrode material to a metal with a lower boiling point, and/or a change in surface temperature of the nozzle, and/or a change of the nozzle geometry inducing a given flow pattern and quenching rate, and/or a change in the position of the carbon-containing gas acting as a quench, and/or the insertion of a quenching surface within the plasma torch tailflame, and/or alternate source of catalyst as illustrated in FIGS. 2 and 3A, all result in modifying and controlling the position of CNT formation. Thus the

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CNT formed may be single-walled, multi-walled (depending mainly on the size of metal particles), and the lengths of the tubes may be affected by any of these changes.

Please replace paragraph [0032] with the following amended paragraph:

[0032] The present invention can involve the use of a plasma torch 1 as described in U.S. Pat. No. 5,147,998 on which a water-cooled nozzle assembly is added for carbon-containing gas injection. Typically, the material for the nozzle is tungsten when using tetrachloroethylene (TCE) as a carbon source gas. The electrodes used in the demonstration experiment were coated with tungsten, although electrode surfaces containing either Fe, Ni, Co, Cr, Mo, Pd, Pt, Ru, Rh, Hf and Gd should also show significant catalytic effects.

Please replace paragraph [0033] with the following amended paragraph:

[0033] Using TCE as a carbon source gas, an evaporator 23 is used to transform the liquid TCE 22 (at room temperature) to a gas carried in heated lines at 200°C. with a helium or argon flow 19. Flowrates used are typically 20 standard litres per minute (slpm) of helium and 0.05 to 0.54 mol/min TCE. Higher power DC plasma torches or inductively coupled thermal plasma torches (TP-ICP) can provide the flexibility to inject the liquid TCE directly into the torch. In such cases, nanoparticles of catalyst can also be incorporated into the liquid feed and simultaneously injected into the plasma.

Please replace paragraph [0034] with the following amended paragraph:

[0034] The plasma torch 1, nozzle 2 and carbon/carrier gas 4 feed lines are assembled to a reactor chamber 17 made of stainless-steel with water

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cooling_7 using a double wall system. Provision is made for access inside the chamber for product recovery on the walls and/or on a collecting plate/receptacle. For continuous operation, further provision should be made for product removal during plasma torch operation. The reactor chamber is to be operated at pressures between 200 and 800 Torr He. Experiments the results of which are shown in FIGS. 6 to 13 were made at 200 Torr He, while the experiments for which the results are shown in FIG. 14 were made at 500 Torr He, and those for FIG. 17 were made at 200 Torr Argon. Provision is made for pumping of the off gases_8 using a water ring vacuum pump 25 in the scheme using TCE as the carbon source gas. Provision is also made at the reactor outlet for off gas cooling_9 before its transport to the vacuum pump. Using the scheme of TCE carbon source, a chlorine separation/recovery system 27, 28, 29, 30, 31 and 26 is used at the outlet of the vacuum pump.

Please replace paragraph [0035] with the following amended paragraph:

[0035] Helium or argon gas is supplied to the main plasma torch 5 gas inlet at a volumetric rate of typically 200 to 225 slpm. This rate is very much dependent on the plasma torch employed. In the experiments described herein, a plasma torch sold by PyroGenesis Inc. model RPT-2, 100 kW high enthalpy plasma torch was used. The use of other torches would dictate the rate. Plasma torch operation also requires water cooling lines and electrical power line connections 6. Typically, TP-ICP plasma torch systems require much lower flowrates.

Please replace paragraph [0038] with the following amended paragraph:

[0038] The type and flow rate of plasma gas can then be adjusted to the desired values. TCE flow is admitted to the evaporator 23 and injected into the

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torch nozzle 2 at a desired flow rate. Adjusting the electric current supplied to the plasma torch sets the quantity of metal vapor in the main plasma stream. Tests were made with arc current at 350 A.